

One-Dimensional Hydrogen Atom

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One-Dimensional Hydrogen Atom

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The quantum-mechanical system which consists of a particle in one dimension subjected to a Coulomb attraction (the one-dimensional hydrogen atom) is shown to have a ground state of infinite binding energy, all the excited bound states of the system having a twofold degeneracy. The breakdown of the theorem that a one-dimensional system cannot have degeneracy is examined. The treatment illustrates a number of properties common to the quantum mechanics of one-dimensional systems.

1. INTRODUCTION

HE one-dimensional hydrogen atom consists of an electron moving in the onedimensional potential -e/|x|. In the standard treatment of this problem in the literature only wave functions of odd parity are derived, i.e., wave functions which change sign under the reflection $x \to -x$. It is clear that such functions do not form a complete set since no function of even parity can be expanded in a series of them. Further it is a general result of the Sturm-Liouville problem that for a one-dimensional system the bound state of lowest energy has a nodeless wave function,2 the number of nodes in the bound state wave function increasing by one as we move up the energy scale from one bound state to the next. The treatment mentioned above gives only states with an odd number of nodes, and half the states of the system are omitted. In fact all the levels of the one-dimensional hydrogen atom are twofold degenerate, having an even and an odd wave function for each eigenvalue, except for the ground state which is an even state localized at the point x=0 and having infinite binding energy. We have here an interesting example of a case where the theorem that the energy levels of a one-dimensional system are nondegenerate is apparently violated. The energy levels and wave functions of the onedimensional hydrogen atom will first be discussed in a qualitative manner and we shall then give a mathematical treatment. Finally the reasons for the breakdown of the nondegeneracy theorem will be considered. The present study was occasioned by the importance of the onedimensional hydrogen atom wave equation in the theory of the exciton in a high-magnetic field.³

2. QUALITATIVE DISCUSSION

The wave equation for the system is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} - \frac{e^2}{|x|}\psi = E\psi.$$
 (2.1)

The solution of this equation for the regions x>0 and x<0 is straightforward, but because of the pole in the potential function at x=0, it is not immediately obvious how the solutions in the two regions should be joined together at the origin. This difficulty may be resolved by approaching the actual potential as the limit of a nonsingular potential V(x), say, having the form shown in Fig. 1. The Coulomb potential has been rounded off in a symmetrical manner at some small cutoff distance x_0 so as to remove

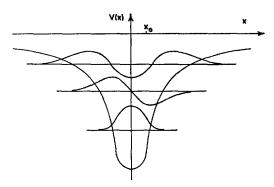


Fig. 1. The modified Coulomb potential V(x) and its three lowest eigenstates.

¹S. Flügge and H. Marschall, Rechennethoden der Quantentheorie (Springer-Verlag, Berlin, 1952), p. 69.

²E. C. Kemble, The Fundamental Principles of Quantum Mechanics (Dover Publications, New York, 1958), p. 124 et sea.

⁸ R. Loudon and R. J. Elliott (to be published).

the singularity. We shall eventually allow x_0 to tend to zero to reproduce the original potential. The detailed form of the rounding off does not affect the conclusions reached about the one-dimensional hydrogen atom; this will be demonstrated in Sec. 3 by considering two types of cutoff.

The wave equation now has the form:

$$\frac{h^2}{2m}\frac{d^2\psi}{dx^2} = [V(x) - E]\psi. \tag{2.2}$$

The forms of the three lowest bound state wave functions are sketched with the potential in Fig. 1. They may be derived by simple qualitative considerations of the solutions of the wave equation and are roughly similar for any nonsingular binding potential.4 The ground state has an even nodeless wave function and the excited states are alternately odd and even. We wish to consider the state of affairs as the cutoff distance x_0 is reduced to zero, when V(x)becomes very large in the region of the origin. For odd states ψ is zero at the origin so that the right-hand side of (2.2) is well behaved as x_0 is decreased, and there is no important change in the character of the odd state wave functions as we proceed to the limit $x_0 = 0$. However in the case of even states ψ is finite at the origin so that $d^2\psi/dx^2$ must be very large there, its magnitude increasing as x_0 is decreased. In the limit $x_0 = 0$, when the Coulomb potential has been restored, $d^2\psi/dx^2$ is infinite at the origin so that the even wave functions have discontinuous slopes at x = 0. The functional form of an even state in the regions x>0 and x<0 becomes the same as that of the odd state which lay next below it in the modified potential but the solutions in the two regions are joined together at the origin to form a function of even parity (see Fig. 5). The odd and even states become degenerate in pairs in the Coulomb limit. The zero in an even wave function at x = 0 should be regarded as a double node since it is formed in the limit by the coalescence of two distinct

An exception to this behavior occurs for the ground state. As V(x) becomes large and negative

close to the origin, E must also become large and negative in order that the magnitude of $d^2\psi/dx^2$ shall not be too large for the ground state wave function to have zero slope at x=0. The wave function therefore becomes concentrated more and more in the region of the origin and in the limit when the original potential is restored, the ground state has infinite binding energy and its probability density is a delta function $\delta(x)$.

The aforementioned qualitative statements will now be justified by solution of Eq. (2.1) and of Eq. (2.2) for two types of cutoff.

3. MATHEMATICAL TREATMENT

We look for bound state (i.e., negative energy) solutions of the wave equation (2.1) and introduce a dimensionless quantity α by taking

$$E = -\hbar^2 / 2ma_0^2 \alpha^2, (3.1)$$

where a_0 is the Bohr length

$$a_0 = \hbar^2 / me^2$$
. (3.2)

It is convenient to change the independent variable in Eq. (2.1) from x to

$$z = 2x/\alpha a_0, \tag{3.3}$$

whereupon the equation takes the form:

$$\frac{d^2\psi}{dz^2} - \frac{1}{4}\psi + \frac{\alpha}{|z|}\psi = 0. \tag{3.4}$$

The wave equation has therefore been reduced to Whittaker's form of the confluent hypergeometric equation. Consider first the region z>0. Equation (3.4) has two independent solutions—one of which diverges like $z^{-\alpha} \exp(\frac{1}{2}z)$ for large z, while the other has a convergent asymptotic form tending to zero as $z^{\alpha} \exp(-\frac{1}{2}z)$. For a bound state we clearly require the solution of Eq. (3.4) which tends to zero as z tends to infinity, and in Whittaker's notation this solution is $W_{\alpha,\frac{1}{2}}(z)$. It is convenient to write down the power series expansion of this function which may be easily obtained by solution of

⁴L. I. Schiff, Quantum Mechanics (McGraw-Hill Book Company, Inc., New York, 1955), p. 32.

⁵ E. T. Whittaker and G. N. Watson, *Modern Analysis* (Cambridge University Press, New York, 1927).

Eq. (3.4) using the method of Frobenius:

$$W_{\alpha, \frac{1}{2}}(z) = \frac{e^{-\frac{1}{2}z}}{\Gamma(-\alpha)} \left\{ z \, {}_{1}F_{1}(1-\alpha,2;z) \right.$$

$$\times \left[\log z + \psi(1-\alpha) - \psi(1) - \psi(2) \right]$$

$$\left. -\frac{1}{\alpha} + \sum_{r=1}^{\infty} \frac{(1-\alpha)_{r}}{r!(r+1)!} A_{r} z^{r+1} \right\}, \quad (3.5)$$

where

$$A_r = \sum_{n=0}^{r-1} \left[\frac{1}{n+1-\alpha} - \frac{1}{n+1} - \frac{1}{n+2} \right] \quad (3.6)$$

and

$$(c)_r = \frac{\Gamma(c+r)}{\Gamma(c)}. (3.7)$$

The function $\psi(s)$ is the logarithmic derivative of the gamma function

$$\psi(s) = \frac{d}{ds} [\log \Gamma(s)] = \Gamma'(s) / \Gamma(s)$$
 (3.8)

and ${}_{1}F_{1}(1-\alpha, 2; z)$ is just the usual confluent hypergeometric function:

$$_{1}F_{1}(1-\alpha,2;z) = \sum_{r=0}^{\infty} \frac{(1-\alpha)_{r}}{(2)_{r}} \frac{z^{r}}{r!}.$$
 (3.9)

It is clear from the series expansion (3.5) that $W_{\alpha,\frac{1}{2}}(z)$ is finite at z=0 but that it normally has infinite slope at this point and thus is usually unsuitable for a wave function. An exception to this behavior occurs, however, when α is a positive integer, for in this case both $\Gamma(-\alpha)$ and $\psi(1-\alpha)$ become infinite and we must consider the limit of $W_{\alpha,\frac{1}{2}}(z)$ as α tends to a positive integer N. Now as $\alpha \to N$,

$$\psi(1-\alpha) \to 1/(\alpha-N). \tag{3.10}$$

Further we may write

$$\Gamma(-\alpha) = \Gamma(-\alpha + N + 1) /$$

$$[-\alpha(1 - \alpha) \cdots (N - \alpha)]. \quad (3.11)$$

Hence:

 $\lim_{\alpha \to N} \psi(1-\alpha)/\Gamma(-\alpha)$

=
$$(-1)^{N+1}\Gamma(N+1)$$
 $(N=1, 2, \cdots)$. (3.12)

All the terms in the numerator of Eq. (3.5) remain finite at positive integral α except for $\psi(1-\alpha)$ so that

$$\lim_{\alpha \to N} W_{\alpha, \frac{1}{2}}(z) = (-1)^{N+1} \Gamma(N+1)
\times e^{-\frac{1}{2}z} {}_{1}F_{1}(1-N, 2; z). \quad (3.13)$$

The confluent hypergeometric function appearing in this equation is simply related to an associated Laguerre polynomial as follows:

$$_{1}F_{1}(1-N, 2; z) = -L_{N}^{1}(z)/N!N, \quad (3.14)$$

so that we have finally:

$$\lim_{\alpha \to N} W_{\alpha, \frac{1}{2}}(z) = (-1)^N e^{-\frac{1}{2}z} z L_N^{-1}(z) / N. \quad (3.15)$$

The function on the right of the above equation is well behaved in the region of the origin and is a satisfactory bound state wave function. We have therefore shown that an acceptable bound-state solution of (3.4) can be formed only when α is a positive integer. The bound-state energies as given by Eq. (3.1) are just the Balmer energies, showing that the one-dimensional and three-dimensional hydrogen atoms have common energy levels.

For the case z>0 we have shown that the wave functions of the one-dimensional hydrogen atom are

$$\psi = Be^{-\frac{1}{2}z} z L_N^{-1}(z),$$

$$z = 2x/Na_0 \quad (N = 1, 2, \dots), \quad (3.16)$$

where B is a normalization constant. Similarly for z < 0 it may easily be shown that:

$$\psi = Ce^{\frac{1}{2}z}zL_{N}^{1}(-z), \qquad (3.17)$$

C being another normalization constant.

We now require to join together the two solutions, Eqs. (3.16) and (3.17), at the point z=0. Since the potential of the problem is invariant under the reflection $x \to -x$, we may insist that the wave functions be either even or odd functions of x. Now Eqs. (3.16) and (3.17) have finite slopes at z=0 and, since the potential has a singularity at this point, there is some ambiguity as to how the solutions should be joined together. In particular it is not clear whether or not even states are permissible. This difficulty may be resolved as was suggested in Sec. 2 by considering the one-dimensional

⁶ Erdélyi, Magnus, Oberhettinger, and Tricomi, *Higher Transcendental Functions* (McGraw-Hill Book Company, Inc., New York, 1953), Vol. 1, p. 261.

hydrogen atom potential as the limit of a nonsingular potential function, a process which also shows that the ground state of the system has been missed in this analysis.

Consider then the problem with a slightly different potential, viz.

$$-e^2/(a+|x|),$$
 (3.18)

where a is a positive quantity very much smaller than the Bohr length a_0 , and which we shall eventually allow to tend to zero so as to reproduce the original potential. The shape of the function is shown in Fig. 2. For large |x|, Eq. (3.18) is little different from $-e^2/|x|$ but the new potential remains finite at x=0 instead of having a pole.

The wave equation is still of the form (3.4) but the variable is now

$$z' = 2(a+x)/\alpha a_0$$
 for $x > 0$,
 $z' = -2(a-x)/\alpha a_0$ for $x < 0$. (3.19)

There is therefore a lower bound of $2a/\alpha a_0$ to the range of values which |z'| can take. The modification we have made to the potential is such that the potential energy of the electron is higher at all points and we may therefore expect the energy levels of the system to be raised slightly above the Balmer energies. Referring to (3.1) we see that the values of α for which eigenfunctions can be formed will be slightly higher than the positive integers. This may be expressed conveniently by defining the quantum defect δ_N of a level to be the difference between the value of α to which it corresponds and the integer N close to α :

$$\delta_N = \alpha - N. \tag{3.20}$$

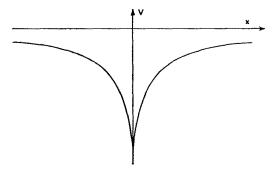


Fig. 2. The potential described by Eq. (3.18).

For $a \ll a_0$ we shall have $\delta_N \ll 1$, and $\delta_N \to 0$ as $a \to 0$.

The bound-state wave function is still $W_{\alpha,\frac{1}{2}}(|z'|)$ given by (3.5). The quantity α is not now integral so the function has infinite slope at z'=0, but this does not matter since the point z'=0 is not included in the physical domain of z'. The solutions for positive and negative x can be joined together at x=0 to form both even and odd wave functions. For an odd state we require

$$W_{\alpha, \frac{1}{2}}(2a/\alpha a_0) = 0 (3.21)$$

while for an even state,

$$\frac{d}{dz'} \left[W_{\alpha, \frac{1}{2}}(z') \right] = 0, \tag{3.22}$$

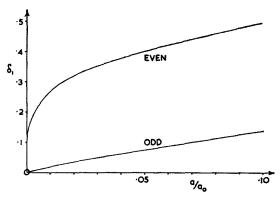


Fig. 3. Variation with a/a_0 of the quantum defects of the two states whose quantum numbers α tend to unity as a/a_0 tends to zero. The even-state quantum defect falls to zero very steeply close to the origin.

when evaluated at $z'=2a/\alpha a_0$. These conditions give the eigenvalues of the system for a given value of a. Using Eq. (3.5), we keep only the terms which are dominant when $z=2a/\alpha a_0$ is very small and α is close to a positive integer. The eigenvalue conditions then become:

Odd state:

$$\psi(1-\alpha)2a/\alpha a_0 - 1/\alpha = 0. \tag{3.23}$$

Even state:

$$\log(2a/\alpha a_0) + \psi(1-\alpha) = 0. \tag{3.24}$$

Using Eqs. (3.10) and (3.20), the quantum defects are given by

Odd state:

$$\delta_N = 2a/a_0. \tag{3.25}$$

Even state:

$$\delta_N = -\lceil \log(2a/Na_0) \rceil^{-1}. \tag{3.26}$$

In Fig. 3 we show how the quantum defect δ_1 varies with a/a_0 for both the odd and the even states. δ_N behaves in a similar manner for the other values of N. The curves were calculated using the complete expression (3.5) for $W_{\alpha, \frac{1}{2}}(z)$ and not the approximate Eqs. (3.25) and (3.26), which hold only at the lower end of the a/a_0 scale, where $\delta_1 \ll 1$.

In addition to these series of odd and even states having their quantum numbers α close to the positive integers, there is another state having α close to zero. For such a value of α , $\psi(1-\alpha)$ is no longer an important term in (3.5)

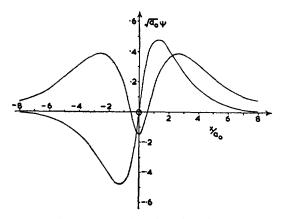


Fig. 4. The two wave functions for which α tends to unity as a/a_0 tends to zero. The value of a/a_0 here is 0.1 and the quantum defects for the odd and even states are 0.14 and 0.50, respectively.

and $1/\alpha$ becomes the dominant term in α . Hence for this case the eigenvalue conditions (3.21) and (3.22) become

Odd state:

$$(2a/\alpha a_0) \log(2a/\alpha a_0) - 1/\alpha = 0.$$
 (3.27)

Even state:

$$\log(2a/\alpha a_0) + 1/2\alpha = 0. \tag{3.28}$$

Equation (3.27) has no solution for $a \ll a_0$, so that there is only one state having $\alpha \ll 1$. This even state is the ground state in the potential (3.18). Since for N=0, α is equal to the quantum defect δ_0 , Eq. (3.28) can be regarded as an equation for the quantum defect of the ground

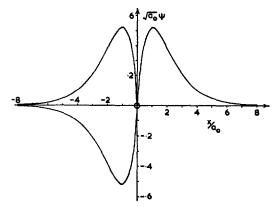


Fig. 5. The two wave functions having the first Balmer energy. For positive x the wave functions are superimposed. The wave functions of Fig. 4 transform continuously into the above pair as a/a_0 changes from 0.1 to zero.

state. It may be solved by iteration, a first approximation being obtained by removing the α from the logarithmic term.

Since the quantum defect for the even state is always larger than that for the corresponding odd state (see Fig. 3), the states alternate between even and odd as we move up the energy scale with an even state lowest. Figure 4 shows the odd and even states for which $\alpha \to 1$ as $a/a_0 \to 0$, for the particular value $a/a_0 = 0.1$. A rather large value of a/a_0 has been chosen so as to show clearly the shape of the even wave function in the region of the origin.

We now wish to obtain the solution to the onedimensional hydrogen atom problem by taking the limit $a \rightarrow 0$. We observe that however small a value of a we may choose, it is still possible to find values of α such that (3.23) and (3.24) are satisfied, the required values of α tending to the positive integers as $a \rightarrow 0$. Hence in the limit a=0 there exist pairs of degenerate odd and even states having the Balmer energies, whose wave functions for positive and negative x are given by Eqs. (3.16) and (3.17), respectively, joined together at x = 0 to form a function of the correct parity. Figure 5 shows the pair of wave functions having the Balmer energy corresponding to N=1. The final normalized expressions for the wave functions are:

Odd states:

$$\psi = [2/a_0^3 N^5 (N!)^2]^{\frac{1}{2}} \times \exp(-|x|/Na_0)xL_{N^1}(2|x|/Na_0). \quad (3.29)$$

(3.30)

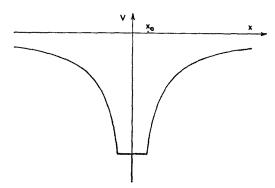


Fig. 6. The truncated Coulomb potential.

Even states:

$$\psi = [2/a_0^3 N^5 (N!)^2]^{\frac{1}{2}} \times \exp(-|x|/Na_0)|x|L_{N^1}(2|x|/Na_0).$$

Remarks similar to the aforementioned apply also in the case of the ground state. As $a \to 0$, $\alpha \to 0$ so that in the limit a=0 the ground state has infinite binding energy. It is easily seen by inspection of (3.4) that the ground-state wave function is $\exp(-\frac{1}{2}|z|)$. The normalized ground-state wave function is therefore,

Ground state:

$$\psi = \lim_{\alpha \to 0} \exp(-|x|/\alpha a_0)/(\alpha a_0)^{\frac{1}{2}}$$
 (3.31)

We note that $|\psi|^2 = \delta(x)$ so that the ground state wave function is localized at the origin.

These results have been derived by modifying the one-dimensional hydrogen atom potential to (3.18) and later taking a limit to restore the original wave equation. Other types of modification to the potential may be used and as an example we consider briefly the potential form shown in Fig. 6, where the Coulomb potential has been cut off at radius x_0 to form a well of depth $-e^2/x_0$ for $|x| < x_0$. We shall eventually take the limit $x_0 \to 0$. In the exterior region $|x| > x_0$ the solutions of the wave equation are just the functions $W_{\alpha, \frac{1}{2}}(z)$ as shown. In the interior region $|x| < x_0$ the wave equation is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} - \frac{e^2}{x_0} = E\psi.$$
 (3.32)

This has both odd solutions

$$\psi \sim \sin\left[\frac{2m}{\hbar^2} \left(E + \frac{e^2}{x_0}\right)\right]^{\frac{1}{2}} x \tag{3.33}$$

and even solutions

$$\psi \sim \cos \left[\frac{2m}{\hbar^2} \left(E + \frac{e^2}{x_0} \right) \right]^{\frac{1}{2}} x. \tag{3.34}$$

The solutions in the two regions are joined up by matching logarithmic derivatives at the boundary $x = x_0$. For the interior wave functions for very small x_0 , we have

Odd states: At $x = x_0$,

$$\left(\frac{1}{\psi}\frac{d\psi}{dx}\right) = \frac{1}{x_0}.$$
 (3.35)

Even states: At $x = x_0$,

$$\left(\frac{1}{\psi}\frac{d\psi}{dx}\right) = -\frac{2}{a_0}.\tag{3.36}$$

The logarithmic derivatives of the exterior wave functions at $x=x_0$ may be calculated by using the series expansion (3.5) and retaining only the dominant terms for small x_0 and α close to an integer. Equating the logarithmic derivatives at $x=x_0$ then gives equations similar to (3.23) and (3.24), from which quantum defects can be calculated. It is straightforward to show that the quantum defects for the even states are the same as for the previous potential (3.18) being given by Eqs. (3.26) and (3.28) with α replaced by α 0. For the odd states the quantum defect varies quadratically with α 0, instead of the linear dependence on α for the previous potential, being given by

Odd states:

$$\delta_N = 2x_0^2/a_0^2. \tag{3.37}$$

The conclusions reached about the energy levels of the one-dimensional hydrogen atom are, however, the same in both cases.

4. THE NONDEGENERACY THEOREM

We have seen that, apart from the ground state, the levels of the one-dimensional hydrogen atom are twofold degenerate. The usual proof of the theorem that a one-dimensional system cannot have degenerate states proceeds as follows. Let V(x) be the potential and E the energy eigenvalue which is common to two wave

functions ψ_1 and ψ_2 . Then

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_1}{dx^2} + V(x)\psi_1 = E\psi_1, \tag{4.1}$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_2}{dx^2} + V(x)\psi_2 = E\psi_2. \tag{4.2}$$

Multiply Eq. (4.1) by ψ_2 and (4.2) by ψ_1 and subtract one from the other to obtain

$$\psi_2 \frac{d^2 \psi_1}{dx^2} - \psi_1 \frac{d^2 \psi_2}{dx^2} = 0, \tag{4.3}$$

that is

$$\frac{d}{dx} \left[\psi_2 \frac{d\psi_1}{dx} - \psi_1 \frac{d\psi_2}{dx} \right] = 0. \tag{4.4}$$

Integrating, one finds that

$$\psi_2 \frac{d\psi_1}{dx} - \psi_1 \frac{d\psi_2}{dx} = \text{constant.}$$
 (4.5)

For large x, ψ_1 , and ψ_2 must vanish if they are to represent bound states, so the constant in (4.5) must be zero. At points where ψ_1 and ψ_2 are nonzero, we may divide by $\psi_1\psi_2$ to obtain

$$d\psi_1/\psi_1 = d\psi_2/\psi_2. \tag{4.6}$$

Integration of this equation leads to

$$\psi_1 = B\psi_2, \tag{4.7}$$

where B is a constant. It therefore appears that ψ_1 and ψ_2 are not independent and the statement that a one-dimensional system can have no degeneracy follows. However, Eq. (4.6) may not hold at points where $\psi_1\psi_2$ is zero and it follows that Eq. (4.7) may hold only between adjacent zeros of $\psi_1\psi_2$. The possibility exists that the value of B may change as we pass through a zero of ψ_1 and ψ_2 . Now such a change in B implies that ψ_1 and ψ_2 cannot both have a

continuous finite slope at the zero and, since the wave functions must satisfy the wave equation, (4.1) or (4.2), this can only be true if the potential V(x) has a singularity at the point where $\psi_1\psi_2$ is zero. The nondegeneracy theorem is therefore not necessarily valid for a potential which has singular points.

This is just the case for the one-dimensional hydrogen atom. The even wave functions have a discontinuity in slope at the origin and this is associated with the fact that the potential of the problem has a pole at x=0. As we move along the x axis the constant B in Eq. (4.7) changes from +1 to -1 when we pass through the origin (see Fig. 5).

Another more commonly quoted example of a one-dimensional system with degeneracy is that of two potential wells separated by an infinite barrier, or separated in space by an infinite distance. Corresponding states in the two wells have equal energies, so that all the levels of the total system are twofold degenerate. The breakdown of the nondegeneracy theorem in this case is due to the fact that if ψ_1 and ψ_2 are degenerate wave functions then $\psi_1\psi_2$ is everywhere zero, due to the infinite barrier or the infinite separation. Equation (4.6) therefore does not hold anywhere and the theorem cannot be proved. For a finite barrier and a finite separation of the potential wells the degeneracy is lifted and the nondegeneracy theorem therefore only breaks down when the finite potential is taken to certain infinite limits. In this respect there is a similarity between the two cases we have considered, in which a one-dimensional system has degenerate energy levels.

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